Rhodium/MonoPhos-Catalysed Asymmetric Hydrogenation of Enamides

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X-ray diffraction: Crystal and Molecular Structure.

Suitable colorless needle-shaped crystals were obtained by recrystallisation from ethylacetate/hexane. A crystal with the dimensions of 0.45 x 0.11 x 0.10 mm was mounted on top of a glass fiber and aligned on a *Bruker*[1] *SMART APEX CCD* diffractometer (Platform with full three-circle goniometer). The diffractometer was equipped with a 4K *CCD* detector set 60.0 mm from the crystal. The crystal was cooled to 100(1) K using the *Bruker KRYOFLEX* low-temperature device. Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed ceramic diffraction tube (*SIEMENS*). Generator settings were 50 KV/ 40 mA. *SMART* was used for preliminary determination of the unit cell constants and data collection control. The intensities of reflections of a hemisphere were collected by a combination of 3 sets of exposures (frames). Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time of 10.0 s per frame. The overall data collection time was 8.0 h. Data integration and global cell refinement was performed with the program *SAINT*. The final unit cell was obtained from the *xyz* centroids of 4653 reflections after integration. Intensity data were corrected for Lorentz and polarization effects, scale variation, for decay and absorption: a multi-scan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*)[2], and reduced to F_o^2. The program suite *SHELXTL* was used for space group determination (*XPREP*).[1]

The unit cell[3] was identified as orthorhombic; reduced cell calculations did not indicate any higher metric lattice symmetry.[4] The $|E|$ distribution statistics were indicative of a non-centrosymmetric space group.[5] The space group $P2_12_12_1$, was derived from the systematic extinctions. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[6,7]

The structure was solved by direct methods with *SIR-97*.[8] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic displacement parameters were refined.

Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2)$ = 0.0855 for 2462 reflections and $R(F)$ = 0.0383 for 2191 reflections with $F_o \geq 4.0\ \sigma(F_o)$ and 187 parameters. A final difference Fourier map did not show residual peaks outside the range ±0.21(4) e/Å^{-3}.

The absolute configuration of the structure of the crystal could not be determined reliably (there are only elements in the structure with very small anomalous effects by the used X-ray wavelength): the Flack's[9,10,11,12] **x**-refinement gave an ambiguous result (**x** = 0.4(14)).

The positional and anisotropic displacement parameters for the non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \sum_h[w(\ (F_o^2) - k(F_c^2)\ )^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_0 and F_c are the observed and calculated structure factor amplitudes, respectively; ultimately the suggested *a* (=0.0423) and *b* (= 0.1173) were used in the final refinement.

Crystal data and numerical details on data collection and refinement are given in Table 1. Final fractional atomic coordinates, equivalent displacement parameters and anisotropic displacement parameters for the non-hydrogen atoms are given in Table 2. Molecular geometry data are collected in Table 3. Tables of atom positions, displacement parameters, comprehensive distances and angles and tables of (F_o^2), (F_c^2) and $\sigma(F_o^2)$ are given as supplementary material[*1] for this paper. Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables for Crystallography*.[13]

All refinement calculations and graphics were performed on a Pentium-III / Debian-Linux computer at the University of Groningen with the program packages *SHELXL*[14] (least-square refinements), a locally modified version of the program *PLUTO*[16] (preparation of illustrations) and *PLATON*[15] package (checking the final results for missed symmetry with the *MISSYM* option, solvent accessible voids with the *SOLV* option, calculation of geometric data and the *ORTEP*[15] illustrations)

Results and discussion.

The adopted atom-numbering scheme of the atoms and the configuration are shown in the *PLUTO* drawings of Fig. 1.; the packing of the molecules is shown in the unit cell in Fig. 2.

Each asymmetric unit contains one formula unit molecule with no atom setting at special position.

The orthorhombic unit cell contains four molecules of the title compound. separated by normal van der Waals distances[18] (Fig. 2). Intermolecular hydrogen bonds[19,20,21] (N-H10...O (1/2-*x*, 1/2-*y*, 1-*z*) = 1.972(16) Å (sum of the corresponding van der Waals radii is 2.72 Å)[17] and a weaker C12-H12"…O (1/2-*x*, 1/2-*y*, 1-*z*) = 2.528(19) Å link the molecules into infinite one-dimensional chains along the [100] vector . Also a short intermolecular C8-H8…O interaction is observed (= 2.246(17) Å.

No missed symmetry (*MISSYM*) or solvent-accessible voids were detected by procedures implemented in *PLATON*.[22]

Titel:

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Table 1.
a. Crystal data and details of the structure determination.

Moiety_Formula	
Formula_Weight, g.mol^{-1}	189.26
Crystal system	orthorhombic
Space group, no.[24]	$P2_12_12_1$, 19
A, Å	9.0712(7)
B, Å	10.7364(9)
c, Å	10.9977(9)
V, Å^3	1071.09(15)
è range unit cell: min.-max., deg; reflections	2.65 - 27.49 ; 4653
Formula_*Z*	4
SpaceGroup_*Z*	4
Z' (= Formula_Z / SpaceGroup_*Z)*	1
ρ_{calc}, g.cm^{-3}	1.174
F(000), electrons	408
μ(Mo Kα), cm^{-1}	0.74
Color, habit	colorless, needle
Approx. crystal dimension, mm	0.45 x 0.11 x 0.10

b. Data collection.

ë(Mo Kα), Å	0.71073
Monochromator	Graphite
Measurement device type	*CCD* area-detector diffractometer
Detector Area resolution (pixels / mm)	4096 x 4096 / 62 x 62 (binned 512)
Temperature, K	100(1)
Measurement method	φ- and ω-scans
θ range; min. max., deg	2.65, 27.50
Index ranges	h: -11→11; k: -13→13; l: -14→14
Min.- Max. absorption transmission factor	0.9673 – 0.9926
X-ray exposure time, h	8.0
Total data	9351
Unique data	2462
Data with criterion: ($F_o \geq 4.0\ \sigma\ (F_o)$)	2191
$R_{int} = \sum [\lvert F_o^2 - F_o^2\ (\text{mean})\rvert] / \sum [F_o^2]$	0.0358
$R_{sig} = \sum \sigma(F_o^2) / \sum [F_o^2]$	0.0377

c. Refinement.

Number of reflections	2462
Number of refined parameters	187
Final agreement factors:	
$wR(F^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$	0.0855
Weighting scheme: *a, b*	0.0423, 0.1173
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
And $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \sum (\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert) / \sum \lvert F_o\rvert$	0.0383
For $F_o > 4.0\ \sigma\ (F_o)$	
Absolute-Structure parameter Flack's **x**	0.4(14)
GooF = S =$[\sum [w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	1.030
n = number of reflections	
p = number of parameters refined	
Residual electron density in final	
Difference Fourier map, e/Å^3	-0.24, 0.21(4)
Max. (shift/ó) final cycle	<0.001
Average (shift/σ) final cycle	0.000

Table 2. Final fractional atomic coordinates and equivalent isotropic displacement parameters with s.u.'s in parentheses. Atoms of the Asymmetric Unit.

Non-Hydrogen parameters

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
O	0.32208(11)	0.76888(9)	0.55978(9)	0.0197(3)
N	0.54464(13)	0.67685(11)	0.53621(10)	0.0159(3)
C1	0.70579(17)	0.39983(14)	0.65872(13)	0.0202(4)
C2	0.80701(19)	0.31076(15)	0.62508(15)	0.0264(5)
C3	0.8361(2)	0.28892(16)	0.50370(16)	0.0303(5)
C4	0.76243(18)	0.35607(15)	0.41672(15)	0.0272(5)
C5	0.66106(16)	0.44521(14)	0.44989(13)	0.0201(4)
C6	0.63062(16)	0.46868(13)	0.57155(13)	0.0169(4)
C7	0.52568(15)	0.56760(13)	0.60717(12)	0.0157(4)
C8	0.42591(17)	0.55976(15)	0.69506(13)	0.0200(4)
C9	0.38974(19)	0.44789(16)	0.76956(15)	0.0253(5)
C10	0.2243(2)	0.4316(2)	0.7843(2)	0.0403(7)
C11	0.44535(15)	0.76616(13)	0.51336(12)	0.0156(4)
C12	0.49278(18)	0.86311(14)	0.42322(14)	0.0201(4)

Hydrogen parameters

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
H1	0.6831(19)	0.4145(16)	0.7427(16)	0.023(4)
H2	0.8593(19)	0.2673(16)	0.6865(15)	0.026(5)
H3	0.910(2)	0.2303(17)	0.4816(16)	0.032(5)
H4	0.781(2)	0.3448(17)	0.3327(17)	0.034(5)
H5	0.6114(18)	0.4927(16)	0.3874(15)	0.025(4)
H8	0.3656(19)	0.6319(16)	0.7099(15)	0.021(4)
H9	0.4326(18)	0.4573(16)	0.8511(16)	0.024(4)
H9'	0.429(2)	0.3727(17)	0.7352(16)	0.029(5)
H10	0.175(2)	0.414(2)	0.705(2)	0.048(6)
H10'	0.187(2)	0.506(2)	0.8225(17)	0.041(6)
H10''	0.203(2)	0.360(2)	0.842(2)	0.056(6)
H12	0.4503(17)	0.9437(16)	0.4506(15)	0.025(4)
H12'	0.451(2)	0.8413(17)	0.3470(18)	0.032(5)
H12''	0.597(2)	0.8671(15)	0.4130(17)	0.030(5)
H19	0.6265(18)	0.6846(14)	0.5040(13)	0.008(4)

*) $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a_i}.\mathbf{a_j}$ [25]

Anisotropic (displacement) parameters (Å^2)
Residue: 1.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O	0.0155(5)	0.0218(5)	0.0218(5)	0.0016(4)	-0.0001(4)	0.0019(4)
N	0.0126(6)	0.0164(6)	0.0188(6)	0.0023(5)	0.0031(5)	-0.0002(5)
C1	0.0214(8)	0.0194(7)	0.0199(7)	0.0033(6)	0.0001(6)	-0.0013(7)
C2	0.0254(8)	0.0212(8)	0.0325(8)	0.0084(7)	0.0003(7)	0.0052(7)
C3	0.0315(10)	0.0204(9)	0.0391(9)	0.0023(7)	0.0080(8)	0.0110(7)
C4	0.0336(9)	0.0236(8)	0.0244(8)	-0.0010(7)	0.0057(7)	0.0021(7)
C5	0.0231(8)	0.0174(7)	0.0199(7)	0.0005(6)	-0.0002(6)	-0.0003(6)
C6	0.0154(7)	0.0143(7)	0.0209(7)	0.0010(6)	0.0008(6)	-0.0029(5)
C7	0.0154(7)	0.0144(7)	0.0172(6)	0.0009(5)	-0.0036(5)	-0.0009(6)
C8	0.0190(8)	0.0199(8)	0.0211(7)	0.0015(6)	0.0008(6)	0.0024(7)
C9	0.0273(9)	0.0255(9)	0.0231(8)	0.0069(7)	0.0057(7)	0.0037(7)
C10	0.0308(10)	0.0332(11)	0.0568(13)	0.020(1)	0.0182(9)	0.0027(9)
C11	0.0161(7)	0.0155(7)	0.0152(6)	-0.0039(5)	-0.0031(5)	-0.0022(6)
C12	0.0204(8)	0.0181(8)	0.0218(7)	0.0016(6)	-0.0003(6)	0.0021(6)

Thermal vibration amplitudes (Å^2)

$F(\mathbf{h}) = F_o(\mathbf{h}) \exp\left(-2\pi^2 \sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_i a_i^* a_j^* U_{ij}\right)$ or $F(\mathbf{h}) = F_o(\mathbf{h}) \exp\left(-8\pi^2 U_{iso} (\sin\theta/\lambda)^2\right)$

Table 3. Selected data on the geometry.

Standard deviations in the last decimal place are given in parentheses.

Interatomic Distances (Å)

O	-C11	1.2296(17)	C4	-C5	1.376(2)
N	-C7	1.4193(18)	C5	-C6	1.389(2)
N	-C11	1.3393(18)	C6	-C7	1.479(2)
C1	-C2	1.376(2)	C7	-C8	1.327(2)
C1	-C6	1.389(2)	C8	-C9	1.490(2)
C2	-C3	1.381(2)	C9	-C10	1.520(3)
C3	-C4	1.372(2)	C11	-C12	1.500(2)

Bond Angles (deg.)

C7	-N	-C11	127.83(12)	N	-C7	-C6	111.70(11)
C2	-C1	-C6	120.77(14)	N	-C7	-C8	122.39(13)
C1	-C2	-C3	120.35(15)	C6	-C7	-C8	125.90(13)
C2	-C3	-C4	119.46(16)	C7	-C8	-C9	126.99(15)
C3	-C4	-C5	120.41(15)	C8	-C9	-C10	111.64(15)
C4	-C5	-C6	120.94(14)	O	-C11	-N	123.41(13)
C1	-C6	-C5	118.07(13)	O	-C11	-C12	121.24(13)
C1	-C6	-C7	121.01(13)	N	-C11	-C12	115.33(12)
C5	-C6	-C7	120.88(13)				

Torsion Angles (deg.)

C11	-N	-C7	-C6	156.00(13)
C11	-N	-C7	-C8	-24.9(2)
C7	-N	-C11	-O	5.1(2)
C7	-N	-C11	-C12	-173.26(13)
C6	-C1	-C2	-C3	0.4(2)
C2	-C1	-C6	-C5	-0.2(2)
C2	-C1	-C6	-C7	-177.79(14)
C1	-C2	-C3	-C4	-0.5(3)
C2	-C3	-C4	-C5	0.5(3)
C3	-C4	-C5	-C6	-0.3(2)
C4	-C5	-C6	-C1	0.2(2)
C4	-C5	-C6	-C7	177.77(14)
C1	-C6	-C7	-N	135.61(14)
C1	-C6	-C7	-C8	-43.5(2)
C5	-C6	-C7	-N	-41.89(18)
C5	-C6	-C7	-C8	139.01(16)
N	-C7	-C8	-C9	175.72(14)
C6	-C7	-C8	-C9	-5.3(2)
C7	-C8	-C9	-C10	-136.30(17)

The sign of the torsion angle is positive if when looking from atom-2
to atom-3 a clockwise motion of atom-1 would superimpose it on atom-4.

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